STUDIES ON AMMONIA REMOVAL AND RECOVERY FROM FERTILIZER WASTE

by

VIJAY KUMAR MINOCHA

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DEPARTMENT OF CIVIL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

JANUARY, 1986

STUDIES ON
AMMONIA REMOVAL AND RECOVERY FROM FERTILIZER WASTE

A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of

MASTER OF TECHNOLOGY

by

VIJAY KUMAR MINOCHA

to the

DEPARTMENT OF CIVIL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
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CERTIFICATE

Certified that the work presented in this thesis entitled "STUDIES ON AMMONIA REMOVAL AND RECOVERY FROM FERTILIZER WASTE" by Mr. Vijay Kumar Minocha has been carried out under my supervision and has not been submitted elsewhere for a degree.

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ACKNOWLEDGEMENTS

I express my sincere gratitude to Dr. A.V.S. Prabhakara Rao, who has been a close and valued guide throughout the present work. It is appropriate to mention that his cordial guidance, valuable suggestions, and sound forethoughts has enabled me to achieve this presentable stage.

I am deeply indebted to all Environmental Engineering family members (Faculty members, Research Associates, Students and Staff members) for their active interest, moral support and constant encouragement, directly or indirectly, throughout the present work.

I also most humbly offer my deep sense of gratitude to Dr. (Mrs.) Leela Iyengar who has helped me at all times and has enriched the present work with valuable suggestions and criticisms from time to time.

My heart-felt thanks are extended to Mr. R.C. Adhikari for his kind help during experimental work.

I am extremely thankful to Mr. Rajesh Seth and Dr. (Mrs.) Vijaylaxmi Sharma for their deep involvement, which needs a special mention.

Last but not the least, I place on record my indebtedness and great sense of gratitude for the inspirations, encouragement and unbounded enthusiasm imparted to me through letters by my Mother, Mrs. Sarla Minocha.

- v k minocha

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ABSTRACT

Air stripping is the most simple method of ammonia removal from fertilizer wastewaters. However this process transfers ammonia from liquid phase to gaseous phase. In the present investigation, studies were carried out for the removal and recovery of ammonia.

Batch scale experiments were conducted to study the effect of temperature, pH and influent concentration of ammonia on the percent removal of ammonia. In a continuous flow process removal of ammonia was studied at different wastewater and air flow rates. Results indicated that the removal obtained in continuous flow packed column were much more compared to continuous flow column with diffused aeration. Ceramic raschig rings were used as packing material. At pH 11, and with influent ammonia concentration of 2000 mg/l, maximum attainable extrapolated percent removal of ammonia in packed column were 81, 91 and 99 with simulated wastewater, and 60, 81 and 91 with microbially hydrolysed urea plant effluent at 26 ± 2°C with air flow rates of 180, 300 and 420 $m^3/m^2/hr$ respectively. With experimental data, nomogram was generated relating the three variables viz. simulated wastewater flow rate, air flow rate and percent ammonia removal. For maximum

utilization of air, and if the required ammonia percent removals are less than 68, it was found that air flow rate should be 6 lpm or less. For ammonia removals beyond 68 percent, higher air flow rate will be desired.

The computer program requiring temperature of system, influent concentration of ammonia nitrogen, wastewater flow rate, pH, and desired effluent concentration of ammonia nitrogen as input, was developed to find the theoretical requirements of air for ammonia stripping process.

Phosphoric acid was used to recover stripped ammonia because ammonium phosphates, as compared to ammonium sulphates, are less soluble. It was found, assuming 90 percent efficiency of stripping process, that one litre of commercially available raw grade phosphoric acid was sufficient to absorb the ammonia stripped out from more than 275 litres of wastewater having influent ammonia concentration 2000 mg/l. Crystals of ammonium phosphates can be recovered from the obtained thick slurry.

Generalized economic study was made, and conditions for minimum overall treatment cost, and optimum height of tower were obtained.

1. INTRODUCTION

Man's activity, in general, results in deterioration of the quality of environment, which adversely affects the environmental assimilation and ecological processes. One roadblock in reversing this trend has been the lack of necessary technology to reliably and economically remove the pollutants which are responsible for the degradation of the quality of the environment.

Industrial wastes include the three phases of matter, the gaseous, the liquid and the solid. The liquid wastes coming out of a nitrogenous fertiliser industry generally contains nitrogen in the form of ammonia and urea approximately 2000 mg/l and 1000 mg/l respectively. Presence of urea by itself can be tolerated by fish at much higher levels, but even small quantity of ammonia, either directly or through the hydrolysis of urea, is toxic to aquatic life (Saxena, 1973).

Various compounds containing the element nitrogen are becoming increasingly important in wastewater management programme because of the many effects that nitrogeneous materials can have on environment. Nitrogen, in its various reduced forms, depletes dissolved oxygen levels in receiving waters, stimulates algal growth, exhibits toxicity towards fish life, affects chlorine disinfection efficiency and presents a public health hazard.

Biological and chemical processes which function in wastewater treatment and occur in the natural environment can change the chemical form of nitrogen. Such change may eliminate one deleterious effect of nitrogen while producing, or leaving unchanged, another effect. For example, by converting ammonia in raw wastewater to nitrate, the oxygen depleting and toxic effects of ammonia are eliminated, but the biostimulatory effects may not be changed significantly (EPA, 1975).

Nitrogen control techniques are divided into two broad categories viz. physico-chemical and biological. The first group involves selective ion-exchange, ammonia stripping, electrodialysis, reverse osmosis, electrochemical precipitation and break point chlorination. The latter group involves nitrification, denitrification, intensive algal culturing, activated flocculating algal-bacterial system and simple lagooning.

Nitrification processes are involved with the conversion of organic and ammonia nitrogen to nitrate nitrogen,a less objectionable form for aquatic life. The other processes are involved not merely with conversion of one form of nitrogen into other, but result in the partial or complete removal of nitrogen from the wastewater.

In determining the method which is most suitable for a particular application, consideration must be given to six principal aspects: (1) form and concentration of nitrogen compounds in the process influent, (2) required effluent quality, (3) other treatment processes to be employed,

(4) cost, (5) reliability, and (6) flexibility. Great care must be taken in developing and evaluating alternatives.

Ammonia is transferred from liquid phase to gaseous phase, which is usually dispersed into atmosphere.in conventional ammonia stripping processes. However ammonia is a stable material, and not oxidized to nitrogen oxides in the atmosphere. Ammonia can react with sulphur dioxide and water to form ammonium sulphate aerosol. Since ammonia is highly soluble in water, and very reactive with acids, these can be used to trap ammonia which is coming out from the stripper. Recovered ammonia will be very useful product because of the economic importance of nitrogen compounds. Different methods of ammonia stripping are reported in literature, few of which describe ammonia removal and recovery systems.

In urea plant wastewaters, along with ammonical nitrogen substantial quantities of the highly soluble urea nitrogen is also present which is a stable compound and requires considerable energy to hydrolyse chemically. However, biological systems achieve this without any seeming effort. Micrococcus ureae, Proteus vulgaris and Bacillus pasteurii are among the major group of organisms which actively hydrolyse urea (Stanier, 1962). A fixed film microbial reactor is designed for urea hydrolysis and is functioning in the Environmental Engineering Laboratory of Civil Engineering Department of I.I.T. Kanpur.

Air stripping and recovery of ammonia with sulphuric acid has been studied (Sharma, 1982), but ammonia was absorbed in solution stage. Sufficient data are not available for a practical design of ammonia removal and recovery system. The present work is aimed at studies on conditions for ammonia removal and practical recovery by air stripping in batch and continuous flow systems.

2. LITERATURE REVIEW

2.1. Sources and Types of Pollution:

Fertilizer industry produces liquid, gaseous, and solid wastes, leading respectively to water, air and soil pollution. These are described below.

2.1.1. Water Pollution:

An average sized fertilizer factory produces large quantities of wastes ranging from 2 to 3 mgd which contain variety of pollutants such as the following (Mohanrao, 1973):

1. Carbon slurry (where partial oxidation method is used in the gasification step)
2. Scrubber wastes such as the following depending on the process used for gas purification:
    a) Monoethanolamine (MEA)
    b) Arsenic (As_2O_3)
    c) Potassium carbonate (K_2CO_3)
    d) Caustic (NaOH)
3. Ammonia-bearing wastes from ammonia synthesis unit
4. Urea and ammonia-bearing wastes from the urea synthesis unit
5. Ammonium sulphate waste from the manufacture of ammonium sulphate
6. Phosphates and fluoride containing wastes from phosphoric acid plant

7. Ammonium phosphate and ammonia from ammonium phosphate plant
8. Acidic spillages from sulphuric acid plant
9. Acid from regeneration of cation exchange units
10. Alkali from regeneration of anion exchange units
11. Oil bearing wastes from compressor house of ammonia and urea plants
12. Cooling waters
13. Domestic sewage.

2.1.2. Air Pollution:

The various types of air pollutants associated with the processes of the fertiliser industry are sulphur dioxide, oxides of nitrogen, particulate dust and ammonia.

The main source of emissions of ammonia in the stack gases are from nitrogen fertilizer manufacturing plants. A large amount of ammonia comes out from stripping towers and stripping ponds.

Available diffusion technology can be used to estimate the atmospheric concentration of ammonia at any point down wind of the stripping tower. Calculations were made for the orange country, California stripping tower (EPA, 1975) for low mixing conditions (wind speed 1 m/sec). The resulting surface concentrations at the centre of down wind discharge zone including natural background levels were as follows.

Distance from tower (meter)	91	305	488	975	4877
Surface air concentration of ammonia (mg/m^3)	5.2	1.6	0.6	0.2	0.0006

2.1.3. Soil Pollution:

The fertilizer industry like many other chemical industries discharges solid wastes which, if indiscriminately dumped, would create soil pollution.

In the production of urea, arsenic is used in scrubbing liquors. Strong wastes and sludges bearing arsenic have to be disposed of on land in remote places or barged to the sea. Careless disposal of these and oil bearing wastes will lead to heavy soil pollution.

In the bagging and packing sections, solid waste is generated which, if handled carelessly, would create soil pollution.

2.2. Associated Pollutional Problems of Fertiliser Wastes:

2.2.1. Toxicity to Aquatic Life:

Almost all the components present in the wastewater of a fertilizer factory can affect in one way or the other a stream which receives them. Acids and alkalis can destroy the normal aquatic organisms of a stream and inhibit or prevent its self-purification. They are also lethal to fish and other aquatic lives. Extreme changes in pH in a stream also adversely affects the fish. Although the final wastewater of a fertilizer factory is slightly alkaline in nature, batch dumping of strong acidic liquor may abruptly, though temporarily, lower its pH to even 3 or less (Mohanrao et.al., 1973).

Alkaline nature of a fertilizer waste is primarily attributable to the presence of ammonia and other alkalis, especially potassium carbonate and caustic soda; the amount of the former compounds being much higher than the latter in a composite waste. Ammonia even in small concentrations is very toxic to fish. Reported levels at which acute toxicity is detectable have ranged (EPA, 1975) from 0.01 mg/l to over 2.0 mg/l.

2.2.2. Public Health:

The public health hazard from nitrogen is associated with the nitrate form and is limited principally to groundwater where high concentrations can occur. Nitrate in drinking water was first associated in 1945 with methemoglobinemia, a sometimes fatal blood disorder which affects infants less than three months old. When water high in nitrate is used for preparing infant formulas, nitrate is reduced to nitrite in the stomach after ingestion. The nitrites react with hemoglobin in the blood to form methemoglobin, which is incapable of carrying oxygen. The result is suffocation accompanied by a bluish tinge to the skin, which accounts for the use of the term "blue babies" in conjunction with methemoglobinemia (EPA, 1975).

Ammonia concentration of 280-490 mg per m^3 of air have been reported to cause eye, nose and throat irritation (Culp et.al., 1978). Concentrations of 1700-4500 mg/m^3 must be reached before human or animal toxicities begin to occur (EPA, 1975).

2,2.3. Biostimulation of Surface Waters:

A major problem in the field of water pollution is eutrophication, excessive plant growth and/or algal "blooms" resulting from over-fertilization of rivers, lakes, and estuaries. Results of eutrophication include deterioration in the appearance of previously clear waters, odor problems from decomposing algae, and a lower dissolved oxygen level which can adversely affect fish life.

Four basic factors are required for algal growth: nitrogen, phosphorus, carbon dioxide, and light energy. The absence of any one will limit growth. In special cases, trace micronutrients such as cobalt, iron, molybdenum and manganese may be limiting factors under natural conditions (EPA, 1975).

2.3. Tolerance Limits:

Indian Standards Institution (I.S.I.) has prescribed standards for tolerance limits for liquid effluents of a chemical industry including fertilizers, discharged on land for irrigation, into public sewers, into inland surface waters including rivers and into marine coastal areas. The Table 2.1 is prepared based on relevant I.S.I. standards. I.S.I. has also prescribed standards for emission limits for various air pollutants emitted from nitrogeneous and phosphatic fertilizer plants.

2.4. Nitrogen Removal Processes:

Many processes have been explored for the removal of both oxidized and unoxidized nitrogen. The major processes are nitrification-denitrification, break point chlorination (or superchlorination), selective ion-exchange for ammonium removal, steam stripping, and air stripping for ammonia removal. These are the processes which are technically and economically most viable at the present time.

TABLE 2.1: Tolerence Limits for Liquid Effluents and Inland Surface Waters

Effluent Characteristic			pH	Maximum			
				Ammonical Nitrogen (as N) mg/l	Free Ammonia (as NH_3) mg/l	Nitrates (as NO_3^-) mg/l	Arsenic (as As) mg/l
For inland surface waters subject to pollution	For public water supply and for bathing ghats	IS:2296-1974	6.0-9.0	-	-	50	0.2
	For irrigation	IS:2296-1974	5.5-9.0	-	-	-	-
For effluents discharged on land for irrigation		IS:3307-1977	5.5-9.0	-	-	-	-
For effluents discharged into public sewers		IS:3306-1974	5.5-9.0	50	-	-	-
For effluents discharged into inland surface waters	General limits	IS:2490-1974 (part I)	5.5-9.0	50	-	-	0.2
	For nitrogenous fertilizer industry	IS:2490-1977 (part IX)	5.5-9.5	100	5.0	-	0.2 (for new plants) 1.0 (for existing plants)
For effluents discharged into marine coastal areas		IS:7968-1976	5.5-9.0	50	-	-	0.2

The other removal processes include (Reeves, 1972) electrochemical treatment, electrodialysis, reverse osmosis, distillation, algae harvesting, and land application.

Most of the above mentioned processes remove only ammonical nitrogen. It is known that fertilizer waste coming from urea manufacturing plant, contains substantial amount of urea along with ammonical nitrogen. So the first stage of the treatment involves the hydrolysis of urea to ammonia.

2.4.1. Urea Hydrolysis:

Urea in concentrations found in wastes as such is harmless to aquatic life, although it may lead to eutrophication of receiving waters. But urea is easily hydrolysed to ammonia under natural conditions, which is lethal to fish even in concentrations of 1.2 mg/l.

There are about 200 species of bacteria that can hydrolyse urea into ammonia and carbon dioxide. Micrococcus ureae, Proteus vulgaris and Bacillus pasteurii are among the major types of organisms which actively hydrolyse urea (Stanier et.al., 1962). A microbial reactor consisting of Bacillus pasteurii grown on coal was proposed for the hydrolysis of urea rich fertilizer waste effluents (Smitt et.al., 1976). An active composite obtained from soil, chicken manure and a source of organic carbon in the form of sweet potato flour has been used for continuous conversion of urea to ammonia (Raman, 1979).

An active immobilized microbial reactor with raschig rings as support medium was developed in our laboratory using the enriched culture prepared from chicken manure (Prasad et.al., 1984) for the hydrolysis of urea. It was observed that a source of organic carbon was essential for the maintenance of microbial activity. With simulated urea plant wastewater, even upto influent concentration of 6600 mg/l urea, no inhibition was observed. Studies also indicated that presence of ammonia in the influent upto 1000 mg/l did not inhibit urea hydrolysis (Prasad et.al., 1984).

Experiments were also conducted (Sharma, 1985) with urea plant effluent, percent hydrolysis reduced from 85% to 65% when hydraulic load was increased from 1.57 $m^3/m^2/hr$ to 6.32 $m^3/m^2/hr$. Bioreactor was used continuously for a period of 3 months without any significant loss in activity indicating that no other nutrients apart from a source of organic carbon is required for the maintenance of active attached mixed culture microbes.

2.4.2 Ammonia Removal by Steam Stripping:

Steam stripping is generally preferred when concentration of ammonia is around 3 to 4 percent in the wastewater. Steam requirement for this process is enormous. For example, for a wastewater flow of 3 mgd, estimated quantity of steam required is about 240 tons/hr, which is considered to be uneconomical, if steam is to be specifically generated for this purpose (Bhalerao and Alagarsamy, 1973).

2.4.3 Ammonia Removal by Air Stripping:

Ammonia in the molecular form is a gas which dissolves in water to an extent controlled by the partial pressure of the ammonia in the air adjacent to the water. Reducing the partial pressure causes ammonia to leave the water phase and enter the air. Ammonia removal from wastewater can be effected by bringing small drops of water in contact with a large amount of ammonia-free air. This physical process is termed desorption, but the common name is "ammonia stripping". In a given time, the quantity of ammonia desorbed from a solution depends on (a) concentration of undissociated ammonia, (b) gas-liquid surface area, (c) mass-transfer coefficient, and (d) partial pressure exerted by ammonia in the gas phase. These, in turn, are influenced by environmental and process conditions (Srinath and Loehr, 1974).

In wastewater, either ammonium ions, or dissolved ammonia gas, or both may be present. The equilibrium equation for ammonia in water is expressed by:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad (2.1)$$

Percentage of ammonia nitrogen in the ammonia form (on a molar basis):

$$NH_3 \text{ percent} = \frac{[NH_3]\ 100}{[NH_3] + [NH_4^+]} \qquad (2.2)$$

The equilibrium constant for ammonia (K_b) can be written as

$$K_b = \frac{[NH_4^+]\ [OH^-]}{[NH_3]} \qquad (2.3)$$

The ionic product of water can be related to hydrogen-ion concentration as

$$[H^+]\,[OH^-] = K_w \qquad (2.4)$$

Substituting these last two relationships into the ammonia percentage expression gives

$$NH_3 \text{ percent} = \frac{100}{1 + K_b[H^+]/K_w} \qquad (2.5)$$

The effect of pH on the ammonia concentration can be readily seen from Eq. (2.5). The equilibrium product of ammonia-ammonium ion varies with temperature as given below (Schroeder, 1977).

T °C	0	10	20	30	40	50
$K_b \times 10^5$	1.374	1.570	1.710	1.820	1.862	1.892

At pH = 7, only ammonium ions in true solution are present, while at pH = 12, only dissolved ammonia gas is present, and this gas can be liberated from wastewater under proper conditions.

The combined effect of temperature and pH on the liquid-phase ammonia concentration is shown in Figure 2.1.

Temperature also affects the gas-liquid ammonia equilibrium. The effect of temperature on the Henry's law constant for ammonia is shown in Figure 2.2 (Schroeder, 1977).

Two major factors affect the rate of transfer of ammonia gas from water to the atmosphere (Culp and Culp, 1971): (1) surface tension at the air-water interface, and (2) difference in concentration of ammonia in the water and the air. Surface tension is at a minimum in water droplets when the

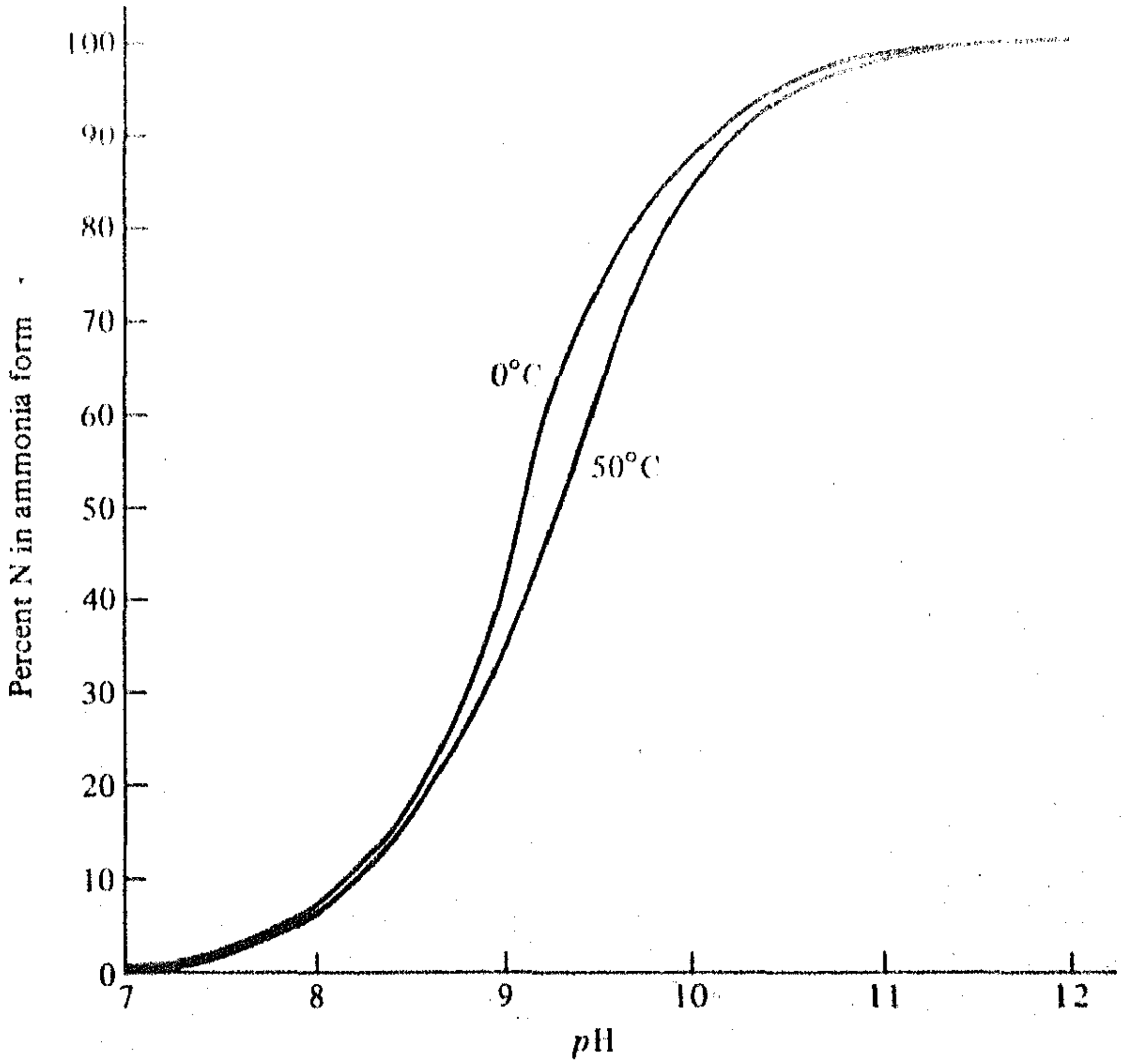


FIGURE 2-1
Percentage of N in ammonia form as a function of pH and temperature.
(Schroeder, 1977)

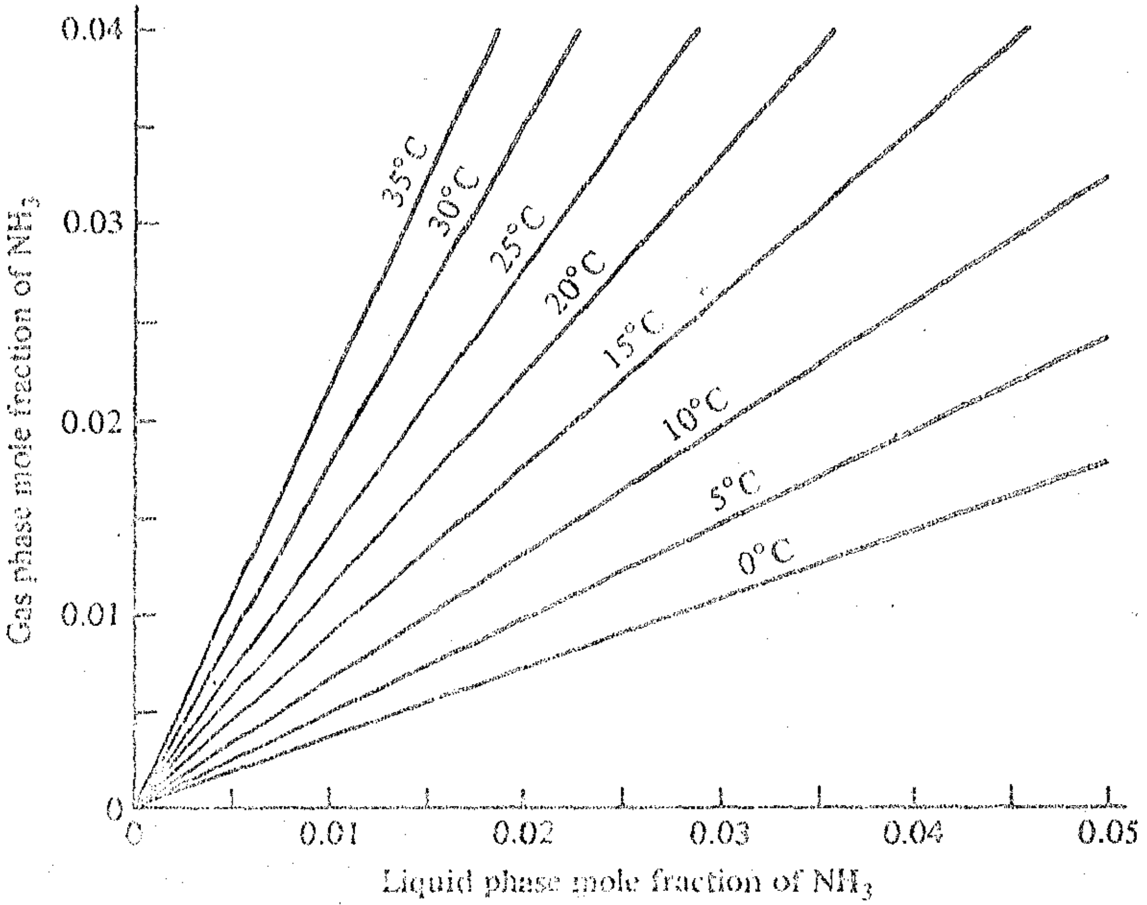


FIGURE 2.2
Liquid- and gas-phase NH_3 mole fractions as functions of temperature.
(Schroeder, 1977)

surface film is being formed, and ammonia release is greatest at this instant. Little additional gas transfer takes place once a water droplet is completely formed. Therefore, repeated droplet formation and coalescing of the water assists ammonia stripping. The ammonia stripping process, then, consists of (1) raising the pH of the water to values in the range of 10.8-11.5, (2) formation and re-formation of water droplets in a stripping tower, and (3) providing air-water contact and droplet agitation by circulation of large quantities of air through the tower.

Unfortunately ammonia is highly soluble in water, and its volatility decreases markedly with decreasing temperatures. For these reasons (O'Farewell et.al., 1972), effective air stripping requires warm temperatures and the use of large volumes of air per unit volume of wastewater.

2.4.3.1. Theoretical Considerations:

The desorption of ammonia from waters involves the contacting of a liquid and a gas phase. With wastewaters, the units may be spray towers, packed column aeration towers, or diffused air systems. One phase usually flows counter-current to the other in a manner such that both the phases are in contact. Ammonia being transferred from the liquid to the gas phase must pass through the interface. It is difficult to measure accurately either the length of the transfer path or the time of contact. It may be assumed (Srinath and Loehr, 1974) that both phases are separated and that transfer resistance layers are formed on either side of the boundary. It is in these layers, or films, that the greatest amount of resistance for mass transfer is encountered. During the removal of ammonia from an aqueous solution by air stripping, the greatest resistance to mass transfer occurs in the transfer from the liquid to the gas phase because of the high solubility and ionization of ammonia in water.

During ammonia removal, the molecules of ammonia escape from the liquid phase and the undissociated ammonia in the solution will tend to approach equilibrium with air in contact with the liquid. At equilibrium, the partial pressure of ammonia in air will be equal to the partial pressure of ammonia in solution. At a given temperature and atmospheric pressure, the relationship between the quantity of ammonia removed (ΔC), the concentrations of undissociated ammonia ($C \cdot F$), the interfacial area of exposure (A_i), and the time (Δt), may be expressed as (Srinath and Loehr, 1974)

$$- \Delta C = k \cdot A_i \cdot C \cdot F \cdot \Delta t \qquad (2.6)$$

where k is a coefficient of mass transfer, F is the ratio of the undissociated ammonia to the total ammonical nitrogen in the solution, i.e., $F = NH_3$ percent (given by Eq. 2.5) divided by 100, and C is total ammonical nitrogen present in the solution.

This equation implies that greater quantities of ammonia can be desorbed by increasing the time and interfacial area of exposure and the concentration of undissociated ammonia in the liquid. This relationship is valid only when the gas phase is not saturated with ammonia.

Increase in area of contact can be achieved by spraying in towers, falling film in towers, flow of liquid in thin films over packings in stripping towers, or diffused aeration.

2.4.3.1.1. Batch Systems:

The amount of ammonia removed from a liquid in a diffused aeration system depends on concentration of ammonium nitrogen, pH, temperature, rate of air flow, volume of liquid, duration of desorption, and mass transfer coefficient. Equation 2.6 can be used for batch diffused aeration desorption systems. Because of the difficulty of measuring or estimating A_i, k and A_i can be combined into an operational desorption coefficient, K_D. K_D is system-specific, being dependent on environmental and process conditions. With this modification, Eq. (2.6) may be written as

$$\ln \left[\frac{C_1}{C_2}\right] = K_D \cdot F \cdot (t_2 - t_1) \qquad (2.7)$$

where C_1 and C_2 are the concentrations of total ammonical nitrogen at times t_1 and t_2, respectively.

The partial pressure exerted by ammonia in air is very low. It takes only a very small amount of ammonia desorbed from the liquid to saturate the air. No further desorption takes place after the gas phase has been saturated with ammonia. In diffused air systems, saturation with ammonia takes place within the first few millimeters of the ascent of the air bubbles through the liquid (Srinath and Loehr, 1974). Because this process of saturation is almost instantaneous, the measured duration of ammonia desorption in the diffused air system is, in fact , a measure of the volume of air needed to achieve the observed removal of ammonia.

2.4.3.1.2. Continuous-flow Systems:

At equilibrium, a mass balance on a continuous-flow aeration unit of volume V having a flow rate Ω and total ammonia concentrations C_1 and C_2 in the influent and effluent, respectively, will show

$$(C_1 - C_2)\Omega = K_D \cdot F \cdot C_2 \cdot V \qquad (2.8)$$

V/Ω is the average liquid retention time in the unit and the average time of desorption in a continuous-flow system. Therefore, the change in concentration as a result of desorption may be presented in terms of the hydraulic retention time, (t_{HR}), as

$$\frac{C_1 - C_2}{C_2} = K_D \cdot F \cdot t_{HR} \qquad (2.9)$$

2.4.3.1.3. Variable pH:

Equations (2.6) through (2.9) are valid for systems where F is constant. To examine systems in which ammonia desorption is accompanied by a change in pH, modifications of the equations are necessary. If ammonia is desorbed from the alkaline solution and the pH of the system is not maintained constant, then the pH will decrease, resulting in a decrease in F and in ammonia loss. The decrease in the pH value is linear with respect to time and the decrease in ammonia concentration is logarithmic with time (Srinath and Loehr, 1974)

$$\ln C_t = \ln C_o - a \cdot t \qquad (2.10)$$

$$pH_t = pH_o - z \cdot t \qquad (2.11)$$

where pH_t and pH_o, and C_t and C_o are the values of pH and ammonium concentrations at times t and o, respectively, and a and z are constants.

It would be useful to develop relationships between pH, time, concentration of total ammonia in the liquid, and K_D for predictive and design purposes. Since F is a function of pH, Eq. (2.7) may be rewritten as

$$\begin{aligned} \frac{dC}{C} &= - K_D \, F \cdot dt \\ &= - K_D \, \frac{10^{pH}}{10^{pH} + (k_b/k_w)} \cdot dt \qquad (2.12) \end{aligned}$$

When the rate of aeration and temperature are constant, the values of K_D and k_b/k_w do not vary. Under these conditions, when pH is allowed to fall as ammonia is desorbed, C, pH, and t are the only variables. Combining Eqs. (2.11) and (2.12) results in Eq. (2.13)

$$\frac{dC}{C} = - K_D \, \frac{10^{(pH_o - z \cdot t)}}{(k_b/k_w) + 10^{(pH_o - z \cdot t)}} \cdot dt \qquad (2.13)$$

If pH_1 and C_1 are conditions at time t_1 and pH_2 and C_2 are conditions at time t_2, Eq. (2.13) may be integrated to

$$\ln(C_2/C_1) = \frac{K_D}{z \ln 10} (L_2 - L_1) \qquad (2.14)$$

where

$L_2 = \ln(10^{pH_2} + k_b/k_w)$

and $L_1 = \ln(10^{pH_1} + k_b/k_w)$.

Because z is the slope of the pH-time curve,

$$K_D = \frac{(pH_2 - pH_1)(\ln C_2/C_1)(\ln 10)}{(t_2 - t_1)(L_2 - L_1)} \qquad (2.15)$$

The values of L at different temperatures and pH can be found.

2.4.3.1.4. Use of Henry's Law:

The air bubbles emerging from an ammonia desorption system will be saturated with ammonia, and the concentration of ammonia in the air bubbles will be in equilibrium with the concentration of ammonia in the liquid (Srinath and Loehr, 1974). The quantity of ammonia removed from the liquid will equal the ammonia in the air diffused through the liquid,

$$V \cdot \Delta C = A \cdot \Delta t \cdot p \cdot \rho_a \qquad (2.16)$$

where

V = volume of the liquid

ΔC = change in ammonical nitrogen concentration in the liquid that occurred by desorption in time t,

p = partial pressure of ammonia in air,

ρ_a = density of ammonia, and

A = air flow rate.

According to Henry's law, p is related to the ammonia concentration of the liquid,

$$p = \frac{C \cdot F}{H} \qquad (2.17)$$

where C.F is the free ammonia concentration in the liquid, and H is the solubility coefficient of NH_3. This relationship is system and temperature-dependent. Henry's law must be used with great care when one is dealing with a gas, such as ammonia, having considerable affinity for water. Henry's law is apparently valid for an air-water-ammonia system if corrections are made for the ionization of ammonia in water. By using Eq. (2.17), Eq. (2.16) may be written as

$$V \cdot C = A \cdot T \cdot \frac{C \cdot F}{H} \cdot \rho_a \qquad (2.18)$$

Equation (2.16) can also be written as

$$\frac{dC}{dt} = \frac{A \cdot \rho_a}{V} p$$

Substitution of Eq. (2.17) in above equation, yields

$$\frac{dC}{dt} = \frac{A \cdot \rho_a}{V} \cdot \frac{C \cdot F}{H}$$

or $$\frac{dC}{C} = (\frac{A \cdot \rho_a}{V \cdot H}) \cdot F \cdot dt$$

Integration of above equation, yields

$$\ln \frac{C_1}{C_2} = (\frac{A \cdot \rho_a}{V \cdot H}) \cdot F \cdot (t_2 - t_1) \qquad (2.19)$$

Comparing Eq. (2.19) with Eq. (2.7) it is apparent that K_D is the equivalent of the factors in parentheses in Eq. (2.19). Thus, if H is known or can be estimated, it is possible to use Henry's law to estimate the quantity of air needed for ammonia desorption. If desorption data are available, Eq. (2.19) can also be used to determine values of H.

It is reported (Srinath and Loehr, 1974) that the value of K_D obtained in both laboratory batch and continuous flow units are comparable with those obtained in the large scale studies. So the data obtained from small scale units can be used to estimate the K_D values in large scale batch and continuous flow systems.

Ample works had been documented on air stripping for ammonia removal from sewage effluents. However, comparatively less amount of work has been done on air stripping of high nitrogenous wastes.

Reeves (1972) quoted Kuhn (1956) to have found out that the optimum pH for stripping was 11.0. The loading that yielded the best results was 1.46 to 1.54 m^3/min of air and 0.63 l/sec of wastewater effluent. Also he stated that the best air/liquid ratio was 205 m^3/min/l/sec. Rao et.al. (1971) observed that air stripping is effective for the removal of ammonia from nitrogenous fertilizer wastes. In another study, when the wastewater was passed through a closely packed aeration tower with 3.6 m^3 of air supplied per litre, ammonia nitrogen removal was very effective (more than 95 percent removal) at any pH above 9.0. The removal fell to 91 percent at a pH of 8.9 and to 58 percent at pH of 8.8 (Culp and Culp, 1971).

The presence of urea in wastewater, which is usually present in urea fertilizer waste does not affect the release of ammonia (Sharma, 1982). The treatment with lime to raise the pH is not as effective as the treatment with NaOH (Ramprasad, 1970).

2.4.3.2. Design Considerations:

The major factors affecting design and process performance include tower configuration, pH, temperature, hydraulic loading, tower packing depth and spacing, air flow, and control of calcium carbonate scaling. Detailed discussions of mass and enthalpy relationships, and theoretical mathematical models of the stripping process are available (Roesler et.al., 1971). However, these models are not normally used (Culp et.al., 1978) for stripping tower design, and an empirical procedure is used.

2.4.3.2.1. Tower Configuration:

There are two basic types of towers, counter-current towers and cross-flow towers. It has been found that cross-flow towers are more prone to scaling problems (EPA, 1975).

2.4.3.2.2. pH:

This has a major effect on the efficiency of the process. The pH must be raised to the point where almost all the ammonium ion is converted to ammonia gas.

2.4.3.2.3. Temperature:

A critical factor is the air temperature. The water temperature reaches equilibrium at a value near the air temperature in the stripping tower. As the water temperature decreases, the solubility of ammonia in water increases and it becomes more difficult to remove the ammonia by stripping. The air flow rate must be increased to maintain a given degree of removal as temperature decreases.

2.4.3.2.4. Hydraulic Loading:

When the hydraulic loading rates becomes too high, the good droplet formation needed for efficient stripping is disrupted and the water begins to flow in sheets (EPA, 1975). If the rate is too low, the packing may not be properly wetted, resulting in poor performance and scale accumulation. However the other view (Trulsson, 1979) is that to admit liquid loads that are considerably lower than minimum wetting rate.

2.4.3.2.5. Tower Packing:

The depth of tower packing required for maximum ammonia removal will depend on tower packing selected. If higher removals are desired with maximum utilization of air through the tower, tower packing depth should be atleast 24 ft unless pilot plant data indicate that a lesser depth of specific packing will accomplish the required removal (Culp et.al., 1978).

2.4.3.2.6. Air Flow:

For a given tower height, increase in ammonia removal can be achieved by increasing the air flow. However, there is a practical limit on air flow rate because of the increase in air pressure drop with increased flow rate. This results in higher capital investment for fans and increased power costs. Pressure drop increases exponentially with air flow rate. In general air velocities of 1600 $m^3/min/m^2$ are considered to be the practical upper limit for counter current towers (EPA, 1975). For warm weather conditions, typical air requirements are about 2500 m^3/m^3 for 90 percent removal and 3750 m^3/m^3 for 95 percent removal (Culp et.al., 1978).

2.4.3.2.7. Scale Control:

A factor which may have an adverse effect on tower efficiency is scaling of the tower packing resulting from deposition of calcium carbonate from the unstable, high pH water flowing through the tower. The severity of scaling problem has varied widely (EPA, 1975). This can be controlled by removing ammonia and carbon dioxide from the off-gas from the tower and recycling the air (Kepple, 1974). The process includes an ammonia stripping unit and an absorption unit. Both of these units are sealed from the outside air but are connected by appropriate ducting. The stripping gas, which initially is air, is maintained in a closed cycle. Mist eliminators are necessary between the absorber and stripper to prevent carryover of the ammonia laden moisture from the absorber to the stripper effluent. Because of the higher power requirements (as compared to single-pass stripping), the use of this process may be limited to the liquids with relatively high ammonia concentration.

2.5. Ammonia Recovery:

Ammonia recovery from wastewaters in packed columns was studied (Trulsson, 1979). It was found that concentration of ammonium salt in phosphoric acid solution at a pH of about 6.5 was increased continuously upto 25 percent salt by weight. Trulsson (1979) quoted Dankwerts and Onda to have found that increase in ionic strength of the solution will decrease the solubility, so absorption is favoured by low pH and high ionic strength.

3. MATERIALS AND EXPERIMENTAL METHODS

3.1. General:

Experiments on removal and recovery of ammonia were conducted. The influent was either a solution of ammonium chloride in tap water or the effluent from the fixed film microbial reactor for urea factory waste water. Performance of the fixed film microbial reactor used for hydrolysing urea of the waste water is described in Section 2.4.1.

Ammonium chloride was used as a source of ammonical nitrogen. Tap water was used for making simulated wastewater. Analysis of tap water is given in Table 3.1. A concentration of 2000 mg/l of ammonical nitrogen was used throughout except in the variable concentration experiments. Sodium hydroxide was used to raise the pH of wastewater.

A rubber tube of 6 mm internal diameter carried the supply of air from an air compressor working between 6 Kg/cm^2 to 7 Kg/cm^2. The compressor was operated by an automatic switch to start or stop the compressor unit depending upon the pressure. The flow of air was measured with the help of a rotameter having the capacity to measure the flow between 0 lpm to 16.4 lpm.

3.2. Experiments:

Experiments were made on batch and continuous-flow units.

TABLE 3.1: Analysis of Tap Water

1.	pH	6.8 - 8.2
2.	Alkalinity	450 mg/l as $CaCO_3$
3.	Hardness	220 mg/l as $CaCO_3$, Ca^{++} as $CaCO_3$ = 50 mg/l
4.	Chloride	20 mg/l as Cl^-
5.	Total dissolved solids	440 mg/l
6.	Specific conductivity	800 - 900 µ siemens/cm
7.	Turbidity	Not detectable

3.2.1. Removal and Recovery Studies in Batch Process with Diffused Aeration:

A reactor vessel of 6 litre capacity containing 4 litres of wastewater was placed in a constant temperature water bath.

The pH of the influent wastewater was adjusted to 11.0 just before starting the run. The experimental set up is shown in Figure 3.1.

3.2.2. Removal Studies in Continuous Flow Process with Diffused Aeration:

A perspex column of effective height 140 cm, internal diameter 5 cm was used. The wastewater was filled in the column. The wastewater flow rate was maintained constant throughout the run.

Experiments were conducted at room temperature. The pH of the influent wastewater was maintained constant throughout the run. The experimental set up is shown in Figure 3.2.

3.2.3. Removal Studies in Continuous Flow Packed Column:

A perspex column of 5 cm internal diameter was filled with raschig rings (packing material). The effective height of the packing material was 140 cm. The wastewater was distributed over the randomly packed bed, exposing a large surface for continuous contact of liquid and gas in counter-current flow.

With this arrangement it was possible to examine the effects of rate of aeration, pH, influent concentration of ammonia, and wastewater flow rate on the stripping of ammonia from the wastewater.

These experiments were conducted at room temperature. The pH of the influent wastewater was maintained constant throughout the run. The experimental set up is shown in Figure 3.3.

The characteristics of packing material used were obtained as following:

Surface area of packing material per litre of sample volume = 3000 cm^2 (approximately)

Porosity = 0.67

Number of raschig rings per litre of sample volume = 300 (approximately)

Weight of raschig rings per litre of sample volume = 670 gm

3.2.4. Recovery Studies:

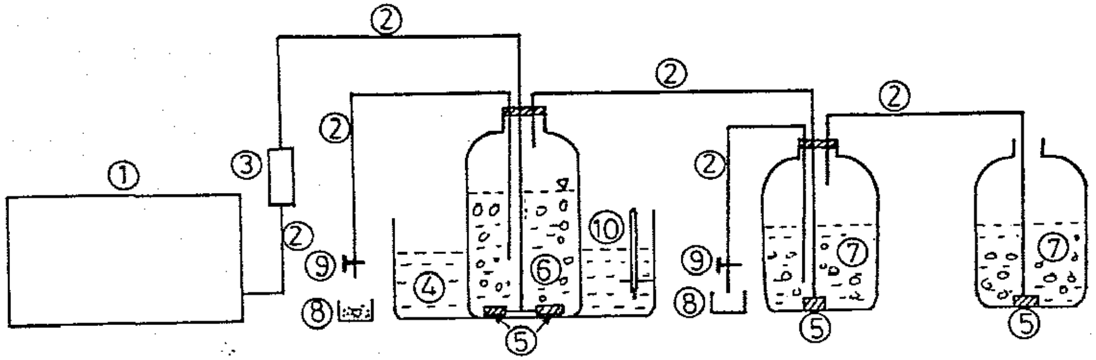


Fig.3·1 Experimental set up for removal and recovery of ammonia in batch process with diffused aeration

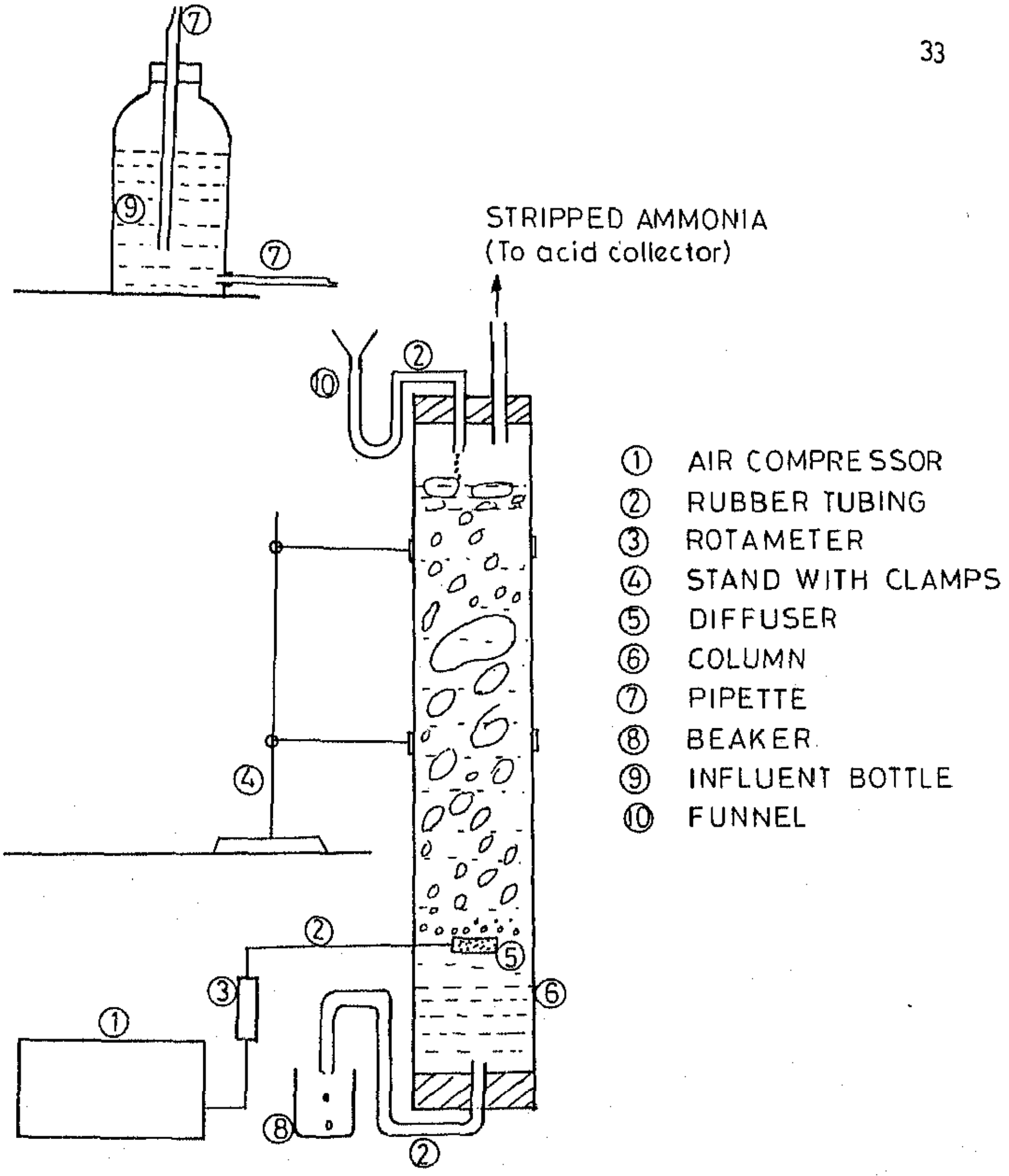


Fig.3·2 Removal of ammonia in continuous flow process with diffused aeration

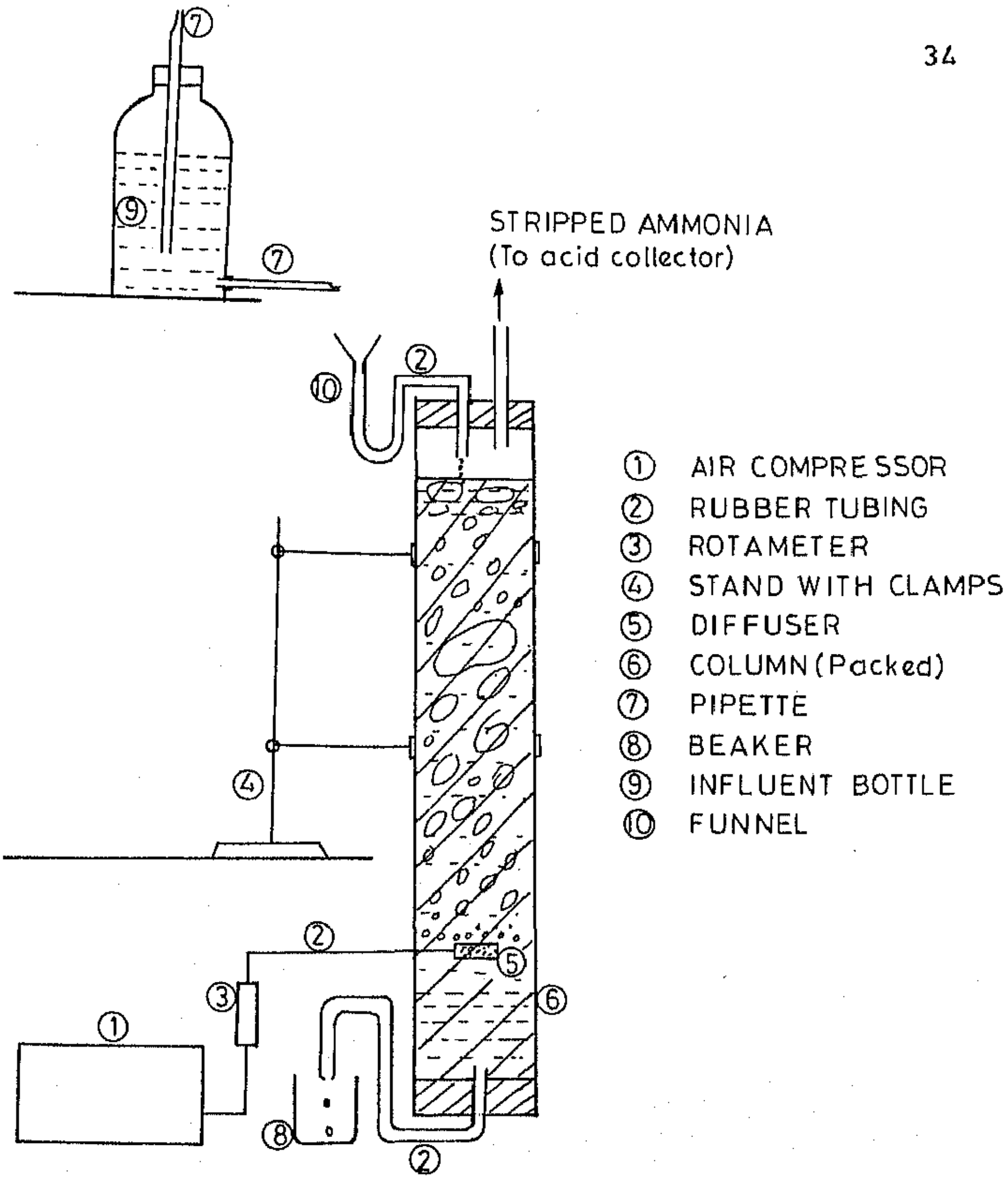
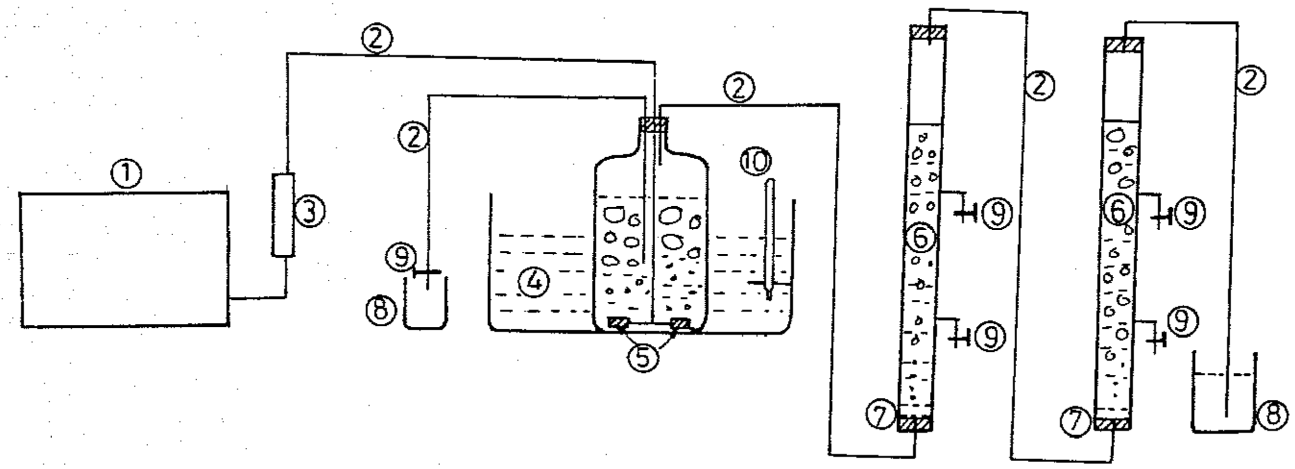


Fig.3·3 Removal of ammonia in continuous flow process (packed column) with diffused aeration

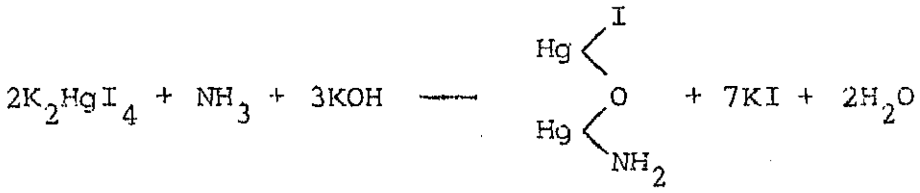


① AIR COMPRESSOR
② RUBBER TUBING
③ ROTAMETER
④ CONSTANT TEMP. BATH
⑤ DIFFUSER
⑥ ACID COLUMN (2·5 cm dia)
⑦ POROUS PLATE
⑧ BEAKER
⑨ VALVE
⑩ THERMOMETER

Fig. 3·4 Recovery of ammonia in batch process

3.3. Method of Analysis:

The ammonia nitrogen in different samples was measured by direct nesslerization. Nessler reagent is a strongly alkaline solution of potassium mercuric iodide (K_2HgI_4 or simply $2KI.HgI_2$). It combines with NH_3 in alkaline solution to form a yellowish-brown colloidal dispersion whose intensity of colour is directly proportional to the amount of NH_3 originally present. The reaction may be represented by the equation (Sawyer and McCarty, 1978)



$$2K_2HgI_4 + NH_3 + 3KOH \longrightarrow \begin{array}{l} \quad\; I \\ Hg\langle \\ \quad\; O \\ Hg\langle \\ \quad\; NH_2 \end{array} + 7KI + 2H_2O$$

This method being very sensitive, appropriate dilutions were necessary to bring down the concentration of samples within the standard curve values.

The yellow colour characteristic of low ammonia nitrogen can be measured with acceptable sensitivity in the wavelength region from 400 to 500 nm when a 1 cm light path is available. The 440 nm wavelength was used consistently for all the samples.

3.4. Reagents:

3.4.1. Nessler Reagent:

Dissolve 100 gm HgI_2 and 70 gm KI in small quantity of water. Add this mixture to a cooled solution of 160 gm NaOH in 500 ml. Dilute to 1000 ml keep the supernatant in coloured bottle.

3.4.2. Standard Ammonia Solution:

Dissolve 0.382 gm of NH_4Cl dried at 100°C in distilled water and dilute to 100 ml. Dilute 1 ml of this solution to 100 ml (1 ml $\cong$ 10 μg N $\equiv$ 12.2 μg NH_3).

3.5. Procedure:

1. Take 10 ml of the suitably diluted (with 0.01N H_2SO_4) sample.

2. Take 10 ml of distilled water for reagent blank.

3. Add 0.2 ml of nessler reagent in each tube, wait for 10 min for the development of yellowish-brown colour.

4. Set the spectrophotometer with reagent blank at 440 nm wavelength. Measure the optical density of the sample.

5. Prepare a calibration curve following the same procedure 1 to 4 but using the standard solutions in place of sample.

The calibration curve obtained is depicted in Figure 3.5.

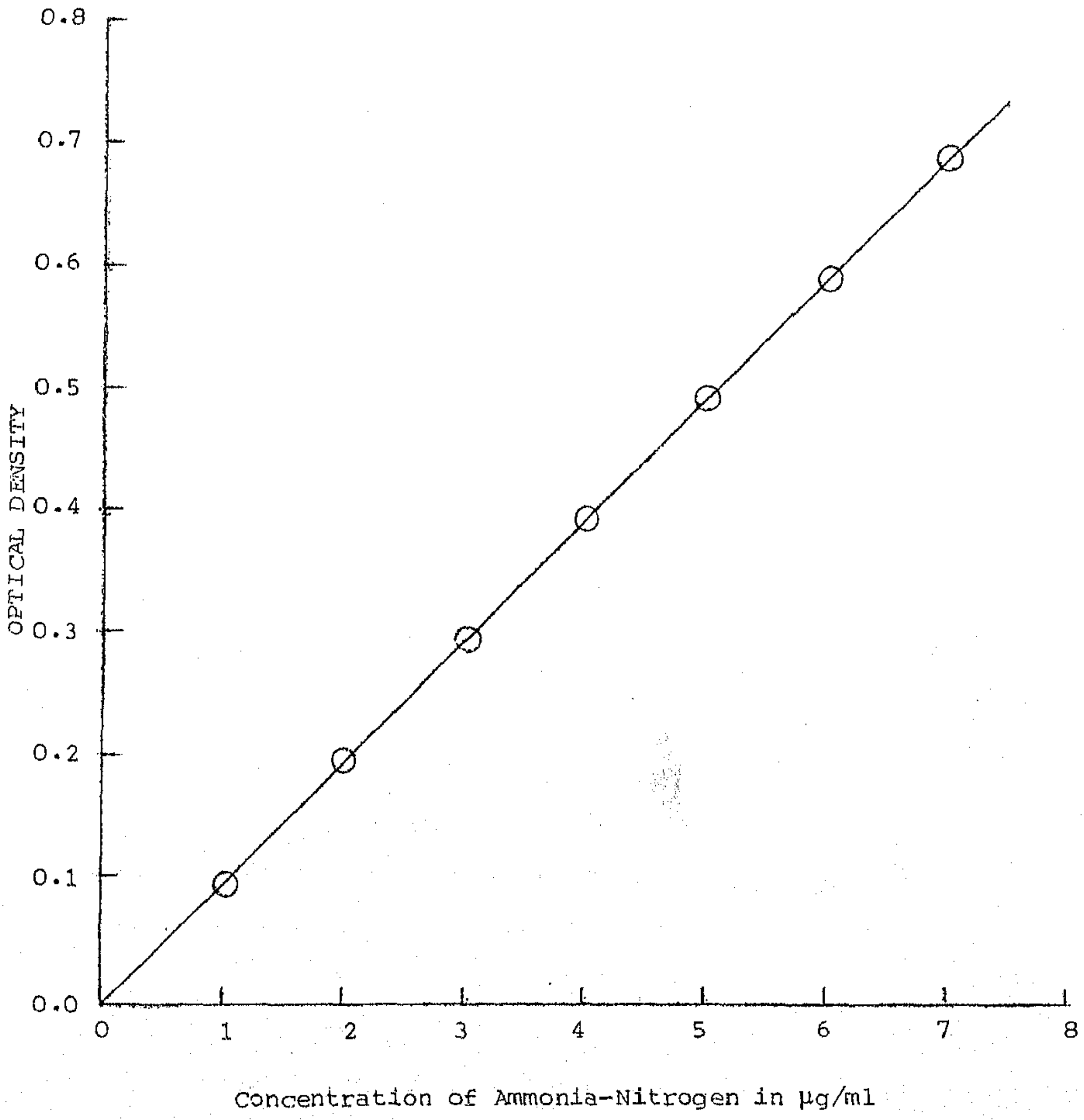


FIG. 3.5 Calibration curve,

4. RESULTS AND DISCUSSIONS

Ammonia removal by air stripping is not new. Earlier experiments have established various conditions regarding air stripping. Further work in removing ammonia from the air by catching it in sulphuric acid solution indicated the feasibility of preventing air pollution during the process. However, recovering ammonia from the ammonium sulphate solution is still a practical problem due to the high solubilities of ammonium salts of sulphuric acid. The experimental results discussed hereafter include some studies on the possibility of not only ammonia removal but also recovery.

Necessarily some of the experiments of earlier workers are briefly repeated to verify and establish conditions for continuation of studies that are extended to facilitate recovery.

In the present investigation, studies were carried out for (i) Removal of ammonia in batch process, (ii) Removal of ammonia in continuous flow process, and (iii) Recovery of ammonia in batch process. The influent was either a solution of ammonium chloride in tap water or the effluent from the fixed film microbial reactor for urea factory wastewater.

The quantities of NaOH required for initial pH adjustment were obtained experimentally, almost 6 Kg of NaOH was required per m^3 of hydrolysed wastewater to attain a pH of 11.

4.1. Removal of Ammonia in Batch Process:

Effect of temperature, pH and initial concentration of ammonia on percentage removal was studied, maintaining air flow rate of 14 lpm.

Experiments were conducted at 25°, 40° and 52°C, and percentage ammonia removals were determined at different aeration time. All these experiments were continued for 6 hours with simulated wastewater, having ammonia concentration 2000 mg/l, and pH 11. The rate of removal of ammonia increased with temperature as expected. Results of these experiments are shown in Figure 4.1.

The decrease in pH of the influent from 11.5 to 10.5 reduced the efficiency for ammonia removal by approximately 5 percent. Further reduction of the pH of the influent to 9.5 reduced the efficiency, as compared to pH 11.5, by approximately 15 percent. All these experiments were conducted for 4 hours with simulated wastewater, having ammonia concentration 2000 mg/l, temperature 25°C. The pH of solution in reactor bottle was monitored, and slope of pH-time curve was obtained as 0.20 per hour.

It was verified that the initial concentration of ammonia has no significant effect on percentage ammonia removal. The initial concentration of ammonia was varied in the range 1000 to 3000 mg/l. Experiments were conducted at 25°C and at an initial pH of 11.

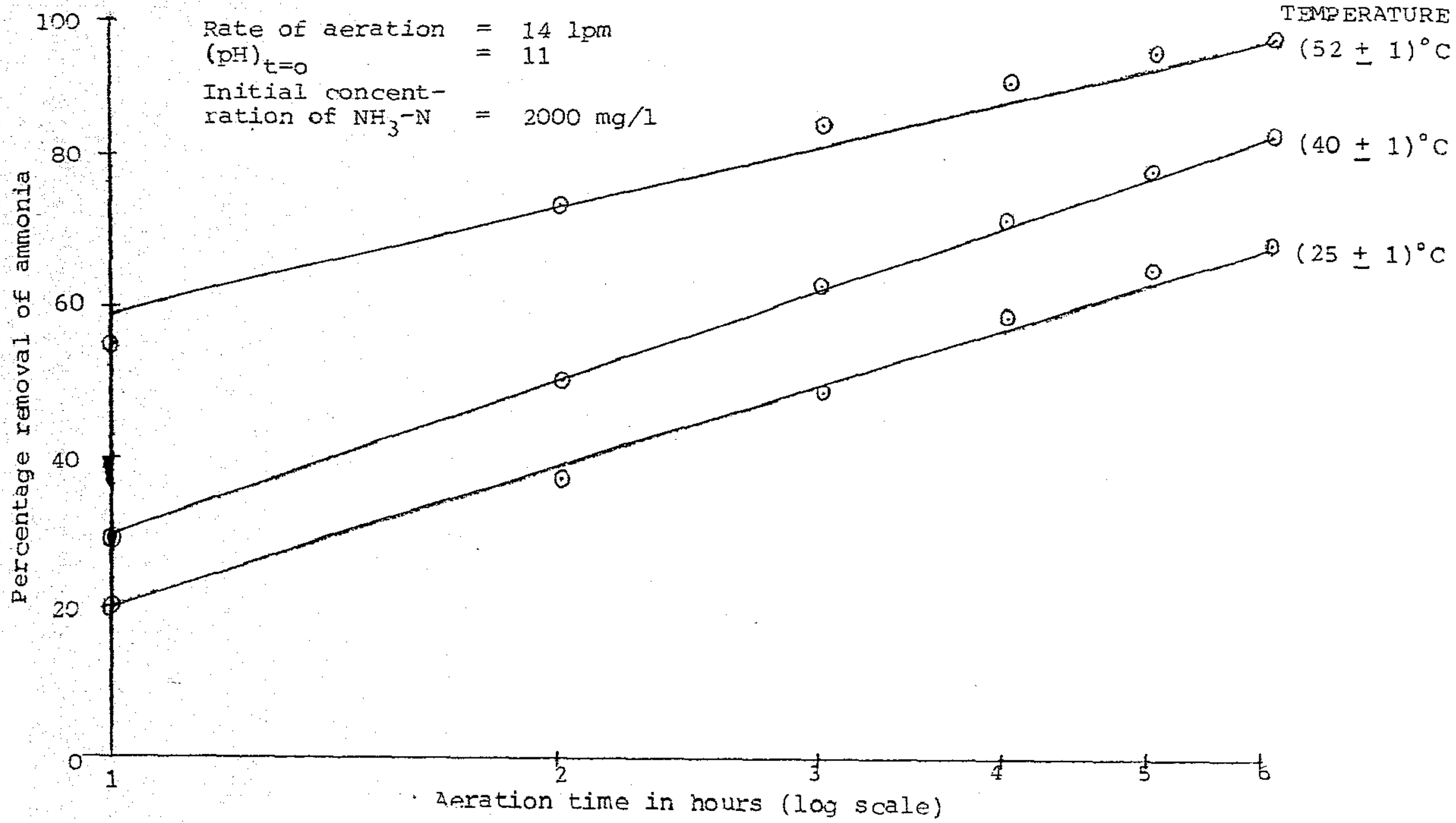


FIG. 4.1 Variation of Percent Removal of Ammonia with Aeration Time at Various Temperatures in Batch Process.

4.2. Removal of Ammonia in Continuous Flow Process:

Percentage removals of ammonia obtained with diffused aeration in continuous flow column were much less in comparison to the packed column under similar conditions. So not much effort was made to study the effect of different process variables for the former case. Moreover, the other serious limitation of this type of arrangement is that it can only function with compressed air and not with conventionally used blowers for aeration.

Column was packed with ceramic raschig rings, characteristics of which are specified in Section 3.2.3. Effective column height of 140 cm, temperature 26 ± 2°C, influent ammonia concentration of 2000 mg/l and pH 11 were maintained throughout. Simulated as well as microbially hydrolysed urea plant wastewater was used as the influent, and was allowed to trickle down in the column. The two basic variables, wastewater flow rate and air flow rate were varied experimentally, and with obtained percentage removals of ammonia, were interplayed to arrive at optimal conditions for stripping process.

Figure 4.2 shows percent ammonia removal with varying wastewater flow rate at different specific air flow rates. From the figure it can be observed that the maximum attainable extrapolated percent removals of ammonia were 81, 91 and 99 with simulated wastewater, and 60, 80 and 91 with hydrolysed wastewater at 26 ± 2°C with air flow rates of 6, 10 and 14 lpm respectively. Maximum attainable percentage removal is lesser with smaller air flow rate because of the fact that

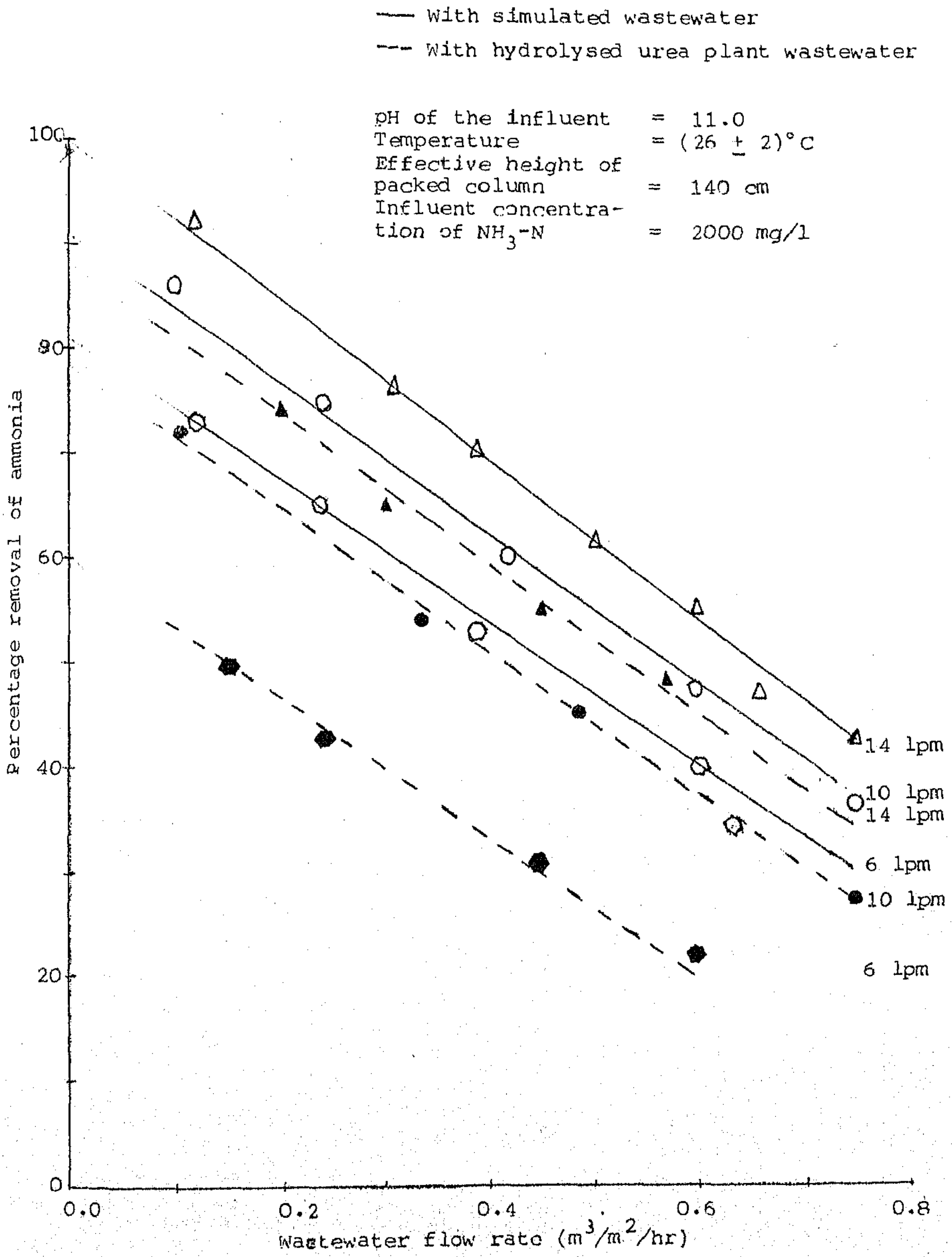


FIG. 4.2 Variation of Percentage Removal of Ammonia with Wastewater Flow Rate at Various Specific Air Flow Ratesin Continuous Flow Packed Column.

ammonia content of air is relatively high in this case and so the driving force for desorption of ammonia is reduced.

Figure 4.3 was prepared to illustrate the patterns of percentage ammonia removal that could result from different combinations of simulated wastewater flow rate and air flow rate. Thus many options can be made to obtain a specific ammonia removal, each requiring different desorption times to accomplish the desired results.

It was also possible to generate a nomogram based on the experimental data. Figure 4.4 shows the nomogram relating the three variables, simulated wastewater flow rate, air flow rate and percent ammonia removal. This nomogram is valid only for prevailing experimental conditions.

Since a dimensionless parameter can be obtained by taking the ratio of simulated wastewater flow rate to air flow rate, all the experimental data were made dimensionless and were plotted against percent ammonia removal. Three different straight lines, intersecting at a point, were obtained, depicting the relationship between dimensionless parameter and percent ammonia removal at various specific air flow rates, as shown in Figure 4.5. At the pivoted point, the value of dimensionless parameter was 10^{-3}, and the percent removal of ammonia was 68 which remained unchanged with variable air flow rate in the range of 6 to 14 lpm (180 to 420 $m^3/m^2/hr$) for prevailing experimental conditions. From the figure it can be observed that for maximum utilisation of supplied air, and if the required ammonia percent

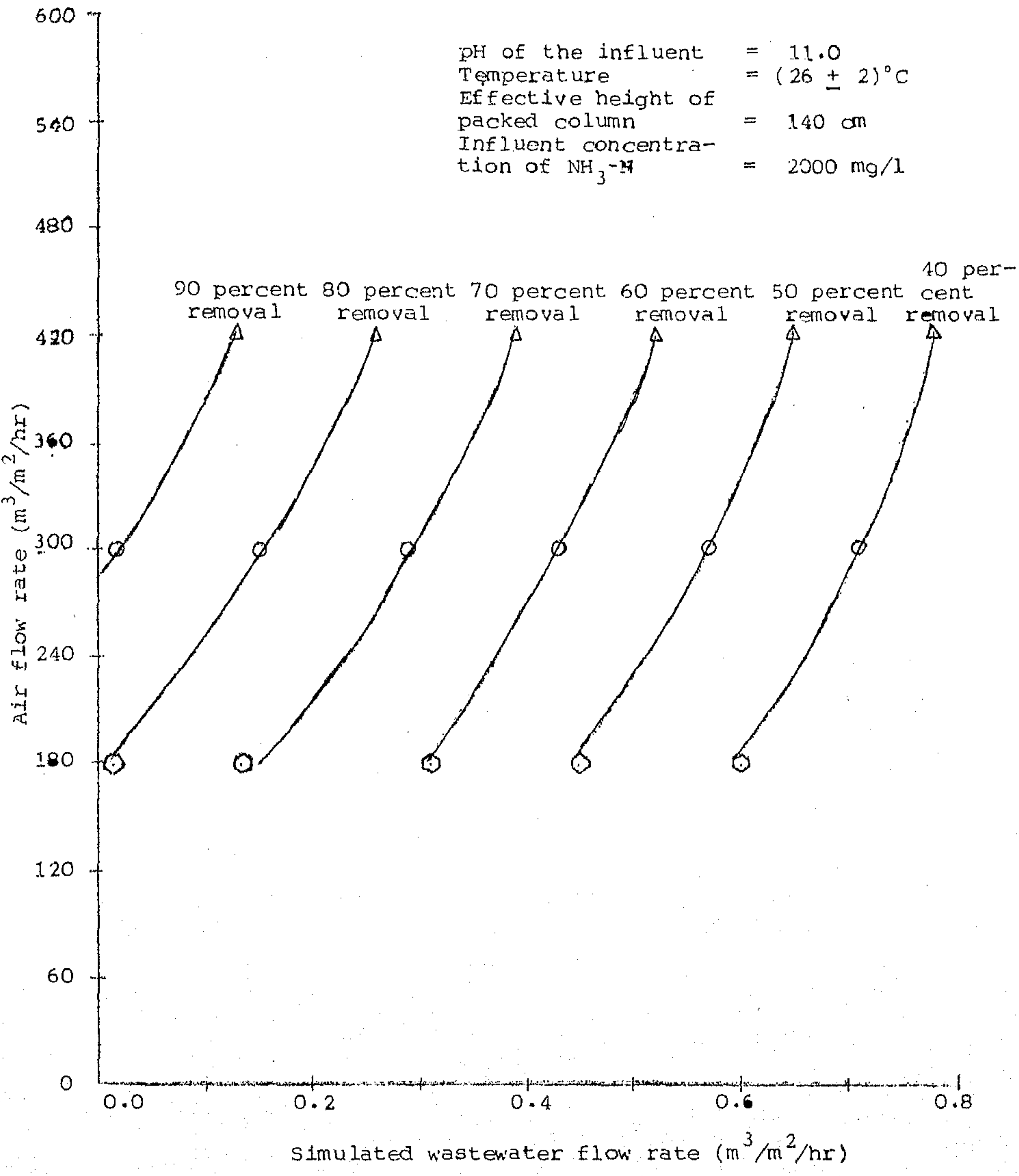
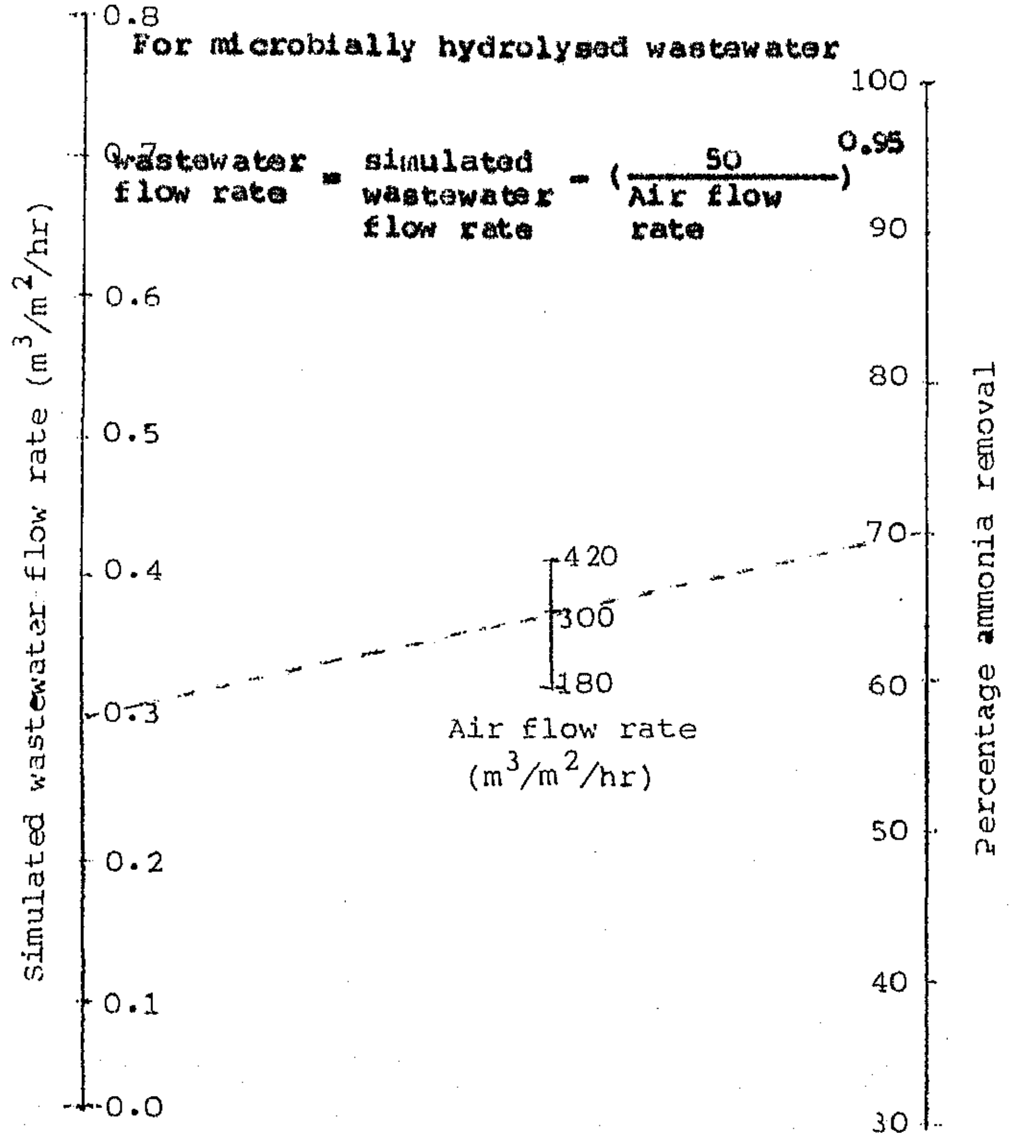
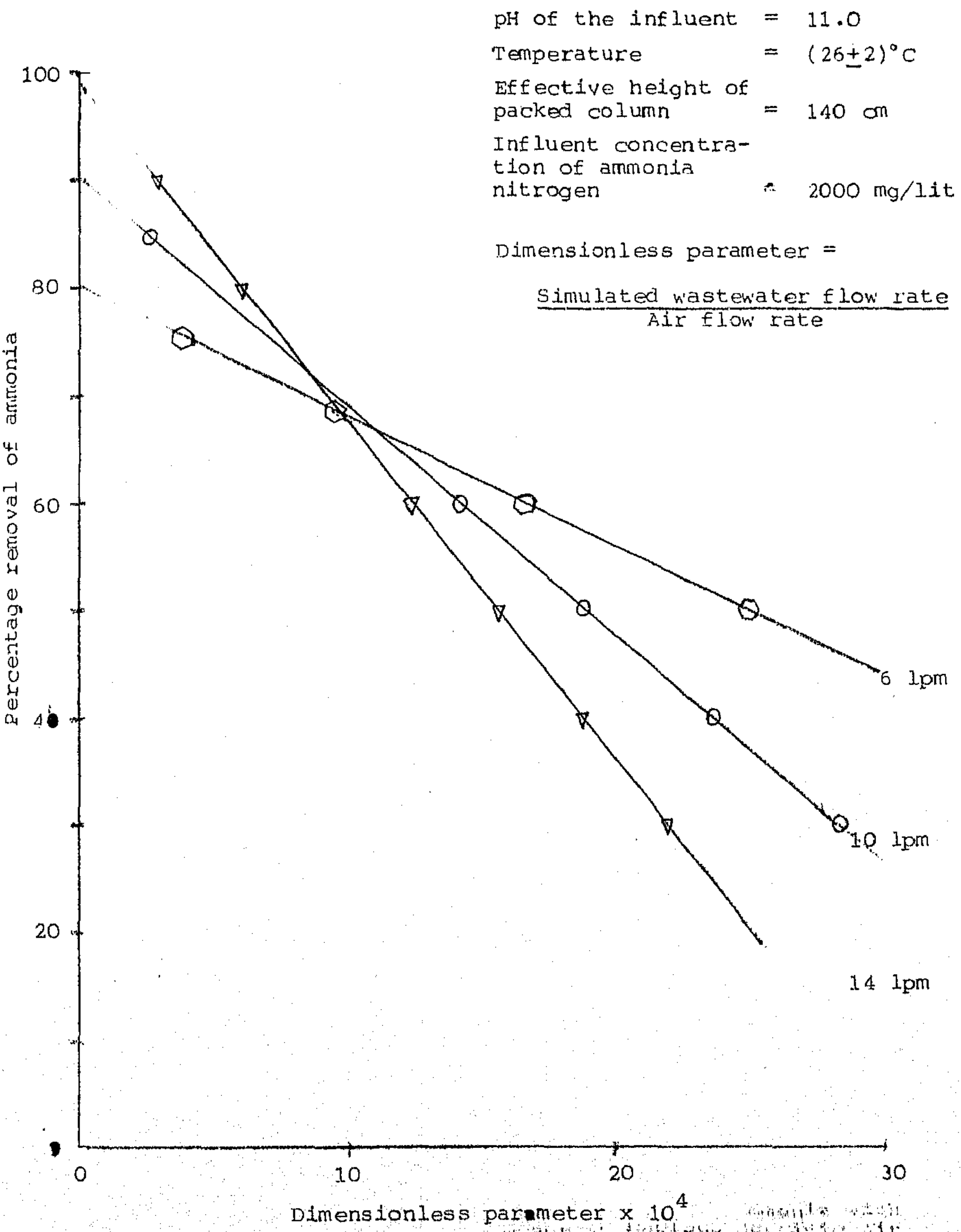


FIG. 4.3 Patterns of Percentage Ammonia Removal for Various Combinations of Air Flow and Simulated Wastewater Flow Ratesfor Continuous Flow Packed Column.



pH of the influent = 11.0
Temperature = (26 ± 2)°C
Effective height of packed column = 140 cm
Influent concentration of ammonia nitrogen = 2000 mg/lit

FIG. 4.4 Nomogram for Continuous Flow Packed Column with Simulated Wastewater.



pH of the influent = 11.0

Temperature = (26±2)°C

Effective height of packed column = 140 cm

Influent concentration of ammonia nitrogen = 2000 mg/lit

Dimensionless parameter = $\frac{\text{Simulated wastewater flow rate}}{\text{Air flow rate}}$

FIG. 4.5 Variation of Percentage Removal of Ammonia with Dimensionless Parameter at Various Specific Air Flow Rates.

removals are less than 68, air flow rate should be 6 lpm or less. On the other hand, if the required ammonia percent removals are more than 68, air flow rate should be higher than 6 lpm.

If sufficient desorption data are not available for a given wastewater, theoretically obtained values of air required may be used. A computer program based on macroscopic mass balance (Schroeder, 1977) and assuming isothermal conditions, is developed to find the theoretical requirements of air for ammonia stripping process (Appendix). This program requires temperature of system, influent concentration of ammonia, wastewater flow rate, pH, and desired effluent concentration of ammonia nitrogen as input. This program is valid in the temperature range 0 to 40°C.

4.3. Recovery of Ammonia in Batch Process:

A reactor vessel with 4 litres of simulated wastewater was taken having ammonia concentration of 2000 mg/l and pH 11. It was observed that almost all the stripped ammonia was absorbed in first of the two collector acid bottles kept in series containing 3 litres of 0.5 N H_2So_4 each. No noticeable change in pH was observed for 6 hours as the quantity of ammonia released fell short of shifting the pH in the first collector bottle itself.

It was felt that it will be uneconomic to crystallize the ammonium sulphate from the solution because of its high solubility in water. Since ammonium phosphates are less soluble, in comparison to ammonium sulphates, phosphoric acid was tried as recovery medium as it will facilitate comparatively easy crystallization. The solubilities of relevant compounds in gm per 100 ml with temperature are as follows (Lurie, 1975)

Ammonium salt of acid	$NH_4H_2PO_4$	$(NH_4)_2HPO_4$	NH_4HSO_4	$(NH_4)_2SO_4$
Solubility	22.7 (0°C)	42.9 (0°C)	100(0°C)	70.6 (0°C)
	36.8(20°C)	68.6(20°C)	-	75.4(20°C)

For the practical recovery, strength of phosphoric acid used was equal to the commercially available raw grade phosphoric acid. Since large amounts of ammonia will be required to neutralize this acid, higher initial concentrations of ammonia (40 gm/l) in influent were used for this experimental study.

It was found that initially all the ammonia was absorbed in first of the two recovery columns kept in series containing 400 ml of phosphoric acid each. When the concentration of ammonia in first column reached the value 200 gm/l, pH of the acid solution was about six, and formation of crystals was noticed in the solution. Since the concentration of ammonia in the reactor vessel by now had come down to about 20 gm/l, and quantity of ammonia being released had also decreased, 40 gm of ammonia (126 gm NH_4Cl) was added to the reactor vessel after six hours of experiment. The released ammonia from the reactor, thereafter seems to have distributed in both the columns containing acid solutions as shown in Figure 4.6. When the concentration of ammonia reached 230 gm/l in first column, the concentration of ammonia in second column was 50 gm/l, which would have otherwise gone to atmosphere in the absence of second column. Though the first column was not fully saturated with ammonia it was not possible to take a sample of acid solution from this column because of clogging of sample port with crystals of ammonium salts of phosphoric acid. After stopping the air supply, it was found that the first acid column was choked with the formed thick slurry.

If the above series of two columns is used for recovery along with the continuous flow packed column for removal of ammonia, and if 90 percent removal of ammonia is achieved in wastewater having influent ammonia concentration 2000 mg/l, it can be calculated with the help of Figure 4.6 that one litre of commercially available phosphoric acid will be sufficient to absorb the ammonia stripped out from more than 275 litres of wastewater.

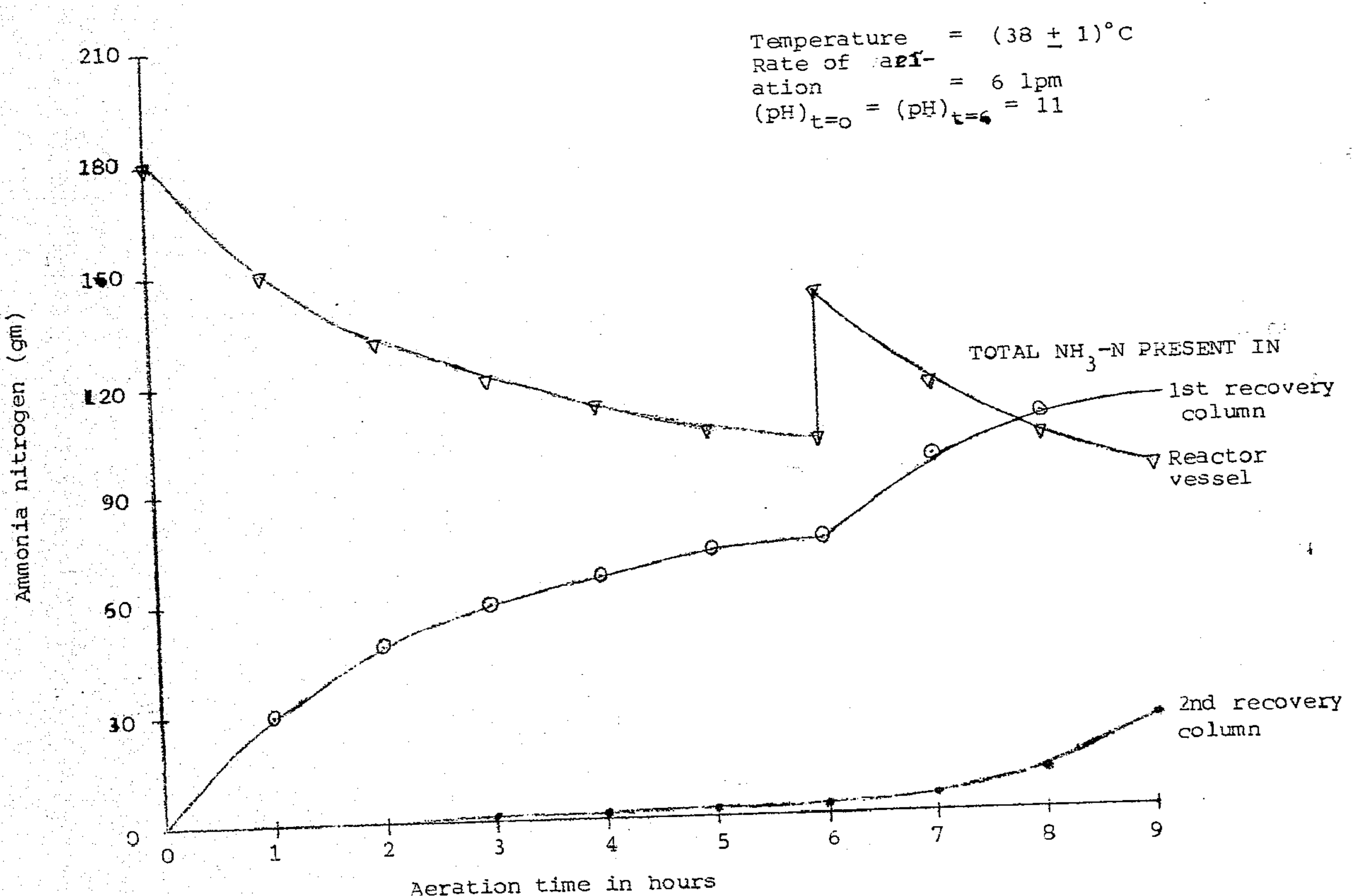


FIG. 4.6 Variation of Ammonia Nitrogen with Aeration Time in Reactor Vessel and Recovery Columns.

5. ECONOMIC CONSIDERATIONS

5.1 General:

Economic feasibility of any particular process relative to alternatives is dependent upon capital, operating and maintenance costs. Capital costs of cross-flow ammonia stripping system, including related yard work, engineering, legal, fiscal, and financing costs during construction, and excluding cost of pH adjustment, and operation and maintenance costs are discussed by Culp et.al. (1978). In a study of counter-current flow ammonia stripping system (Roesler et.al., 1971) percent removal versus height of tower at various G/L values was plotted, and it was obtained that an optimum total treatment cost is achieved around a G/L value of four, where G and L were gas and air flow rates in $Kg/m^2/hr$.

5.2. System Economics:

Considerable laboratory and pilot testing will be necessary to determine which of the alternatives is most suitable and what the process parameter values should be. For almost every situation, there are a number of combinations of process parameters which will satisfy the specified removal condition from the wastewater. To attain a stated degree of treatment, overall treatment cost should always be minimized. Economic considerations for ammonia stripping and recovery are presented here in a qualitative sense. To economize the system, some mathematical tools are used here, along with economics principles. Thus, the basic aims are

(i) To minimize the overall treatment cost

and (ii) To maximize the quantity of recovery product.

5.2.1. Cost Components:

Components of capital, operation and maintenance costs and recovery benefits are dealt here describing their functional relationship with tower height for constant cross-sectional area, influent pH, wastewater flow rate, specified removal of ammonia from influent, and for practical upper limit of air flow rate.

5.2.1.1. Components of Capital Cost:

5.2.1.1.1 Aeration Tower with Foundation:

Construction cost of tower will increase with increase in height of tower. If height of tower is H, the construction cost of tower may be expressed as $a.H^n$, where a, n are constants. From the construction practices, it can be found that n is always greater than one.

5.2.1.1.2 Pumps:

Pumps are used to pump the influent wastewater to the top of tower packing. Cost of pumps is directly proportional to the height of tower, and so, can be represented as b.H, where b is a constant.

5.2.1.1.3 Blowers:

In practices, blowers are used to supply the air. For the counter-current flow towers with film packing, the air pressure drop is obtained from the correlation (Roesler _et.al._, 1971)

$$\Delta P = f \, H \, G^{1.6}$$

where ΔP is pressure drop, f is Fanning friction constant and G is air flow rate. The capital cost of fan can be expressed in terms of pressure drop (Roesler et.al., 1971) as $c_1(\Delta P)^{0.324}$, and so it can be approximated as $c_2 . H^{0.324} . G^{0.52}$. Since practical upper limit of air flow rate is always desired for higher removals, so cost of fan can be represented as $c . H^{0.324}$, where c is a constant.

5.2.1.1.4 Recovery Units:

For specified removal of ammonia from wastewater, construction cost of these units can be designated as d, a constant.

5.2.1.1.5 Packing Material:

This is directly proportional to the height of tower, and so can be expressed as e.H, where e is a constant.

5.2.1.2. Components of Operating and Maintenance Cost:

5.2.1.2.1 Acid:

Acid is required for (i) recovery medium, and (ii) effluent pH adjustment. It is proposed to use phosphoric acid as recovery medium, and any raw quality of H_2SO_4 or HCl, for effluent pH adjustment. Both of these components are design constants for a specified removal of ammonia from the wastewater. The total cost of both types of acids can be designated as A, a constant.

5.2.1.2.2 Pump Power:

For a constant rate of influent, this is directly proportional to the height of tower, and can be expressed as B.H, where B is a constant.

5.2.1.2.3 Fan Power:

This can be expressed in terms of pressure drop (Roesler et.al., 1971) as $C_1 . \Delta P.G$, and so it can be simplified as $C_2 H.G^{2.6}$. Since practical upper limit of air flow rate is always desired for higher removals, so this cost can be expressed as C.H, where C is a constant.

5.2.1.2.4 Cost of Alkali:

Sodium hydroxide or lime can be used for influent pH adjustment. For specified pH of influent wastewater, this can be designated as D, a constant.

5.2.1.3. Recovery Benefits:

For specified removal of ammonia from wastewater, this can be designated as R, a constant.

5.2.2. Problem Formulation and Its Solution:

Two basic components are essential for constructing a problem (i) the objective of the system, and (ii) the constraints imposed on the system. Both the objective and constraints are expressed in terms of controllable variables of the system. The analysis of the model then yields the best course of action that satisfies all the system constraints.

The problem is formulated with height of tower (H) as the basic controllable variable, and all the components are expressed in terms of H and other constants (can be obtained from the latest available similar existing treatment system). Thus, it will reduce to a problem of unconstrained optimization.

From the preceeding discussion, and taking all the factors given in Section 5.2.1, it can be concluded that

Total capital cost, $C_c = a.H^n + b.H + c.H^{0.324} + d + e.H$

or $C_c = a.H^n + c.H^{0.324} + (b + e)H + d$ (5.1)

Total operating and maintenance cost for unit time (say 1 year),

$$\begin{aligned} C_{om} &= A + B.H + C.H + D \\ &= (A + D) + (B + C).H \qquad (5.2) \end{aligned}$$

Recovery benefits $= R$ (5.3)

If 'i' is the inflation factor, we can project the (i) Total capital cost, (ii) Total operating and maintenance cost, and (iii) Total recovery benefits, as follows:

Projected overall cost $C_p = (1 + i)^N.C_c + N(1 + i)^{N-1}.C_{om} - N(1 + i)^{N-1}.R$ (5.4)

where 'N' is the life of the treatment system. For the computations, it is usual practice to take i and N as 0.1 (i.e. 10 percent inflation factor) and 30 years respectively. So, the projected overall cost (C_p) becomes:

$$C_p = 17.45[a.H^n + c.H^{0.324} + (b + e).H + d] + 3\,(\quad 475.9[(A + D) + (B + C).H - R] \qquad (5.5)$$

If the graph of C_p versus H is plotted in the practical limits of H, it is possible to find the H for minimum value of C_p. This value of H is H_o, the optimal value of tower height, and overall treatment system cost corresponding to this height is desired.

Mathematically, the above unconstrained optimization problem can be solved by one of the well known methods (Taha, 1976) viz. Newton-Raphson method, Direct Search method, Steepest Ascent method etc.

For the total cost to be minimum, a necessary condition is

$$\frac{d}{dH}(C_p) = 0, \text{ which yields,}$$

$$17.45[(b + e) + a.n.H^{n-1} + 0.324.c.H^{-0.676}] + 475.9(B + C) = 0 \qquad (5.6)$$

Solution of this equation will yield a set of extreme points. All extreme points, which are in practical range of H are back substituted in equation (5.5) and C_p is obtained. The minimum value of C_p thus becomes the desired value. The value of H, where C_p is minimum, is optimal value (H_o), with respect to economic as well as experimental considerations.

The limitations of such generalized cost estimates must be kept in mind, and process variables for above said system must be based upon the conditions encountered at the specific plants.

6. SUMMARY AND CONCLUSIONS

The initial phase of the present study was devoted to confirm some of the findings of the past researchers and to establish conditions for the present investigation. The results of the laboratory investigation demonstrated the feasibility of air stripping of ammonia from microbially hydrolysed urea plant wastewater and its subsequent recovery as ammonium phosphate crystals using phosphoric acid as collector media. One litre of commercially available raw grade phosphoric acid was sufficient to absorb the ammonia stripped out from more than 275 litres of wastewater having influent ammonia concentration 2000 mg/l assuming 90% NH_3 removal. When influent ammonia concentration was 2000 mg/l, maximum percent removals of ammonia obtained in continuous flow packed column were 81,91 and 99 with simulated wastewater, and 60,81 and 91 with microbially hydrolysed wastewater at 26 ± 2°C with air flow rates of 180, 300 and 420 $m^3/m^2/hr$ respectively and at pH 11. Removals in continuous flow packed column were much more compared to continuous flow column with diffused aeration. In the continuous flow packed column when the ratio of air to simulated wastewater was 1000,the percentage removal of ammonia was 68, and remained unchanged with variable air flow rate in the range of 180 to 420 $m^3/m^2/hr$. A nomogram was generated for prevailing experimental conditions relating the three variables, viz., simulated wastewater flow rate, air flow rate and percent ammonia removal for continuous flow packed column.

The nomogram was found to correlate well with the experimental data obtained using microbially hydrolysed wastewater.

The computer program requiring temperature of system, influent concentration of ammonia nitrogen, wastewater flow rate, pH, and desired effluent concentration of ammonia nitrogen as input, was developed to find the theoretical requirements of air for ammonia stripping process. Assuming height of tower (H) as basic variable, optimum capital, operating and maintenance costs of ammonia stripping and recovery system were worked out in qualitative sense.

7. SUGGESTIONS FOR FUTURE WORK

1. Percentage removals of ammonia in continuous flow packed column should be obtained with varying influent ammonia concentration and column height, and with these data a set of pivoted points can be obtained. This set of points will form the basis of economical design.
2. For continuous flow packed column, the effect of surface area per unit volume of packing material on the removal should be investigated.
3. The cost coefficients should be evaluated for the existing stripping towers, and a model should be prepared to project it for future time.
4. The pH of effluent coming out from stripping column is slightly more than 10. The effluent contains 200-300 mg/l of Total Kjeldal-Nitrogen approximately. To reduce the nitrogen concentration to acceptable limits, use of algal cultures, water hyacinth and direct application on land to yield fodder/vegetables should be investigated.
5. In order to recover the crystals of ammonium phosphates from thick slurry, further work on the design of the recovery system should be done.

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APPENDIX

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C*********************************************************************
C THIS PROGRAM GIVES THE ATR REQUIRMENT(THEORTICAL,ASSUMING
C ISOTHERMAL  CONDITIONS)FOR THE AIR STRIPPING PROCESS USED
C FOR AMMONIA REMOVAL
C*********************************************************************
C*********************************************************************
C   THE OUTPUT GIVES VALUE OF AIR(GAS)REQUIRED FOR THE SPECIFIED
C   REMOVAL (INPUT) IN  LITRE PER SECOND, IT ALSO GIVES THE
C   AVAILABLE  AMMONIA AT GIVEN PH AND TEMPERATURE(INPUT)
C*********************************************************************
       REAL KW,KM,KB,L
       TYPE 100
 100   FORMAT(5X,'TYPE INPUT: PH,  CI,    CE,  T,   WFR,AS
       1    11.5,3700.0,35.0,38.4,17.36')
C*********************************************************************
C      WHERE INPUT IS PH,CI-INFLUENT CONC. IN MG./LIT. CE-EFFLUENT
C      CONC. IN MG./LIT. OF AMMONIA NITROGEN ,T:TEMP. OF THE
C      SYSTEM(LIQUID & AIR) WFR:WASTE FLOW RATE IN LIT./SECOND
C*********************************************************************
       ACCEPT*,PH,CI,CE,T,WFR
 160   KW=10.**(-14)
 10    HION=10.**(-PH)
       if(t.gt.0 .and. t.le.10.)goto110
       if(t.gt.10 .and.t.le.20)goto120
       if(t.gt.20 .and.t.le.30)goto130
       IF(T.GT.30..AND.T.LE.40.)GOTO140
```

```
110   KB=(1.374+.0196*T)/100000
      km=.388+.0257*t
      goto 220
120   KB=(1.57+.014*(T-10))/100000
      km=.645+.0487*(t-10)
      GOTO 220
130   KB=(1.71+.011*(T-20))/100000
      KM=1.132+.0607*(T-20)
      GOTO220
140   KB=(1.82+.0042*(T-30))/100000
      KM=1.739+.0771*(T-30)
220   AMMPER=100./(1.+KB*(HION/KW))
      EFFC=14.0*(CE-(1.0-AMMPER/100)*CI)/17.0
      IF(EFFC.LT.0)GOTO170
      REMOVL=(AMMPER/100.)*CI-EFFC
      AI=CI/(1000.*17.)
      AE=EFFC/(1000.*17.)
      X2=AI/(55.55+AI)
      X1=AE/(55.55+AE)
      Y1=0
      Y2=KM*X2
      L=WFR*55.55
      G=L*(X2-X1)*22.4*((273.+T)/273.)/Y2
      TYPE*,CI,CE,WFR,T,PH
      TYPE*,G,AMMPER
      WRITE(22,250)CI,CE,EFFC,REMOVL,WFR,T,PH,AMMPER,G
```

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